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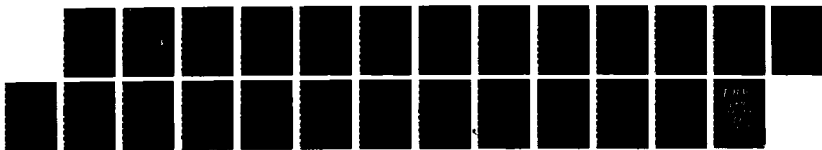
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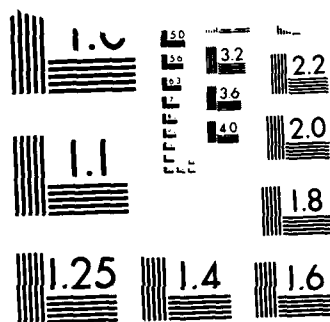
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By

A.B.P. Lever

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# PHTHALOCYANINES

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## Introduction

In 1928, at Grangemouth, Scotland, traces of a blue material were found at the works of Messrs. Scottish Dyes Ltd., during the preparation of phthalimide from phthalic anhydride. This intense blue material was later demonstrated to be ferrous phthalocyanine. Thus was born an industry initially based upon dyes but now rapidly developing into many other fields.

Phthalocyanines (Pc) (Fig.1) are generally blue or green in their normal oxidation state, intensely coloured in the solid, usually with a characteristic purple sheen when crystalline. Numerous X-ray structures have generally, though not exclusively, shown a square planar arrangement of the Pc unit about the central metal atom. Virtually every metallic element, and a few non-metallic elements, form phthalocyanines. The formation of square planar species provides two axial sites at which additional chemistry frequently occurs. In a sense, the phthalocyanines form a Periodic Table of their own in which each MPc has a chemistry dictated by the element and its Pc environment. This therefore provides for a wealth of different applications for these species, tuned by the central ion, by the axial ligation, by substituents in the phthalocyanine ring, and by the phthalocyanine environment [1,2]. There are currently

some 4900 different phthalocyanines known, and some 6000 references discussing them since 1967.

In addition to their extensive use as green and blue colorants for a wide range of paints, textiles, plastics, and metal surfaces, the intense colour of these materials lends itself especially to the production of inks. Most dark blue ink ball point pens are phthalocyanine based.

In the following discussion, we explore some of the uses being developed for phthalocyanines, providing leads to the literature, but certainly not in a comprehensive fashion, given the space available.

#### Electrocatalysis

Metal phthalocyanines are growing in importance as electrocatalysts. Over a decade ago, their use as oxygen reduction catalysts began to develop as a possible replacement for platinum in fuel cell cathodes. CoPc and FePc are especially effective as oxygen reduction electrocatalysts. Both these species can be dispersed in a carbon electrode to generate water or hydrogen peroxide as oxygen reduction product depending upon factors such as pH [3]. Tetrasulfonated iron and cobalt phthalocyanines reduce oxygen in aqueous phase and have been studied as monolayers on ordinary pyrolytic graphite electrodes as a means of investigating detailed mechanisms [4]. Earlier work showing that poorly defined binuclear and polymeric phthalocyanines were better at oxygen reduction than mononuclear phthalocyanines led to the synthesis of well defined soluble (organic solvent), binuclear phthalocyanines, with neopentoxy sidechains, which are also effective at oxygen reduction [5]. Rather unexpectedly a thin film of PtPc has also been shown to be

effective in oxygen reduction [6]. Cobalt(II) phthalocyanine, and, with less activity nickel phthalocyanine, have recently been shown to electrocatalytically reduce carbon dioxide generating formic acid at pH 2-7 [7].

The oxidation of a range of sulphur systems such as thiols, e.g. cysteine and hydrogen sulphide [8] has been studied, especially in Russia using CoPc [9]. Cobalt and iron tetrasulfonated phthalocyanines (MTsPc) are more effective than Mn, Ni or Cu systems. The electroreduction of cystine has also been studied, with MnTsPc being most effective [10]. The oxidation of sulphur dioxide to sulfuric acid, has also been studied catalytically [11] and electrocatalytically [12,13]. Virtually all the first row transition metal phthalocyanines are active with Mn, Fe and CoPc being the most active [12]. Some interesting spectroscopic studies of the reaction of OVPc with hydrogen sulphide have also been reported [14]. Sulphur compound oxidation catalysis has potential use in the clean-up of sulfur-containing effluents. Many other substrates have been oxidised catalytically or electrocatalytically by metallophthalocyanines; among these are included hydrogen peroxide [15] and hydrazine [16].

#### Photovoltaics

Thin-film phthalocyanines on electrodes have potential industrial importance as photovoltaic devices, and in the design of display devices (vide infra) [17]. Thin film sandwich photovoltaic cells composed of a transparent metal electrode, commonly gold, and a thin film of a metal phthalocyanine (e.g. ClAlPc, FAlPc, ClGaPc, ClInPc, VOPc, TiOPc, H2Pc), and a blocking contact, commonly aluminum, have proven to be relatively

efficient (2-10%, photocurrent quantum efficiency) [18,19]. The use of an aluminum phthalocyanine with surfactant substituents (on the aluminum) also seems promising [20]. Other sandwich electrodes which have been studied include a thin film of n-type CdS laid upon In/SnO<sub>2</sub>, with a p-type MPc on the CdS followed by a gold film. Mg and ZnPc are effective in this mode, but, again ClAlPc and ClInPc appear more efficient [21]. Photo-electrochemical cells of the type metal oxide semi-conductor electrode/-sensitizer/redox electrolyte/Pt electrode have been fabricated using metallophthalocyanines as the sensitizer. Here the intent can be the photovoltaic generation of energy with no net change in redox electrolyte, or photo-production of chemical products therein (e.g. water oxidation). Most of the first row transition metal MPcs have been tested in this fashion [22a]. The photoelectric behaviour of Langmuir-Blodgett films of copper phthalocyanine, have also been studied [22b].

#### Photocatalysis

In related studies, MPc systems have been screened as photocatalysts for water reduction to hydrogen [23]. In multi-component sacrificial systems, many main group and transition metal MPcs can photocatalytically reduce methyl viologen, providing a pathway to molecular hydrogen. These molecules are likely to be more chemically stable than analogous porphyrins but the quantum yields are generally very small.

## Molecular Metals

Metal phthalocyanines tend to form crystals in which phthalocyanine molecules pack parallel to one another. If these are 'partially' oxidised, the charge propagates along the chain generating a so-called unidimensional conductor. For example iodine oxidation of CoPc and NiPc lead to CoPcI and NiPcI which contain, formally,  $(MPc)_3^+ I_3^-$  units stacked in a regular fashion. In the former case the oxidation is associated with the cobalt atoms and leads to conductivity comparable with Pt-Pt stacked systems, while in the latter case, oxidation occurs at the ring providing rather different behaviour. Despite the difference in electronic structure, the crystal structures are almost identical [24]. Iodine doped FAlPc and FGaPc also look very promising in this context [25]. Iodine doping is not the only procedure for making these species. Compounds such as  $NiPc(BF_4)_{0.33}$  also have high conductivities [26]. These 'molecular metals' may prove to have industrially useful properties.

## Photoconductivity

There has been immense interest in the photoconductive properties of metallophthalocyanines. Phthalocyanines, such as X-PcH<sub>2</sub> (a polymorph of metal-free phthalocyanine prepared by grinding to a very finely divided state) have photoconductive properties which make them especially useful for photocopying devices. Many commercial photocopiers use phthalocyanine derivatives as the active light sensitive medium, though information on these species is generally buried in the patent literature.

## Electrochromism

Lanthanides and actinides form di-phthalocyanine complexes of general formula  $MPC_2$ . The metal ion is sandwiched between two roughly parallel phthalocyanine units being 8-coordinated by the central nitrogen atoms. Of especial interest is the electrochromic behaviour of many of these species, investigated in particular by Kirin and by Nicholson. Lutetium diphthalocyanine, for example, exists in a range of oxidation states having violet, blue and green and yellow-red colours. Polarisation of an electrode assembly containing  $LuPc_2$  generates a color depending upon the potential applied [27]. Mono-phthalocyanine systems seem less suitable for this purpose, though a recent study of octacyano-phthalocyanines showed electrochromic behaviour for metal-free, zinc and copper species [28]. Other di-phthalocyanines such as  $SnPc_2$  may also be useful. The use of Langmuir-Blodgett films [29] shows promise with metal-free phthalocyanine having been shown to be electrochromic therein [30]. Electrochromic phthalocyanines are being intensely investigated as display devices of considerable industrial promise.

## Chemical Sensors

When a phthalocyanine is placed on, or between, electrode surfaces, some property of this device may 'respond' to the presence of incoming molecules permitting the design of a sensor which may detect such molecules at ppm to ppb levels. In this respect, the semi-conductor properties of the phthalocyanines can be utilised. If a Langmuir-Blodgett film of  $MPc$  is placed on a planar micro-electrode array, a current is obtained when the device is biased. When the film is sensitive to other

chemical molecules, a change in current may be used to monitor their concentration [31]. Such a device is called a chemiresistor [32]. Using an interdigitated microelectrode array and a tetracumylphenoxy substituted CuPc, it is possible to detect ammonia vapour below 0.5ppm, by monitoring current flow. The device is also sensitive to other donor molecules such as NO<sub>2</sub> (1ppm), but not to non-donor molecules such as benzene [32]. Various patents have been awarded for the development of gas sensors (frequently oxygen) which involve MPcs. For example, this is accomplished using a metal-air electrochemical cell, in contact with air, having an anode impregnated with various polymeric MPcs, including Fe, Mn, Co, Ni, Cu, Mo, and also non-polymeric PbPc [33], Fe, Pt and PdPc [34].

A moderately selective sensor for NO<sub>2</sub> (1ppb - 10ppm) is obtained by exposing a PbPc (or H<sub>2</sub>Pc) film, at temperatures above 100°C, to NO<sub>2</sub> and monitoring the change in electrical conductivity [35]. A modification of this technology is the use of a phthalocyanine modified electrode (CoPc/carbon paste) as a detector of hydrazine in chromatography [36].

## Batteries

There is considerable interest in the development of high energy density batteries. Primary and secondary lithium battery systems are under intense development, and both may use phthalocyanines as electrocatalysts. They involve a carbon cathode impregnated with electrocatalyst, and a lithium metal anode. Primary cells (non-rechargeable) use thionyl chloride as 'solvent' and redox active species. The thionyl chloride is reduced at the cathode, with phthalocyanine electrocatalysts, inter alia, being used to increase the discharge rate of such cells.

FePc and CoPc are seen to be effective, but CuPc is much less so. Polymeric (FePc)<sub>n</sub> and (CoPc)<sub>n</sub> species apparently have greater stability [37]. Phthalocyanine catalysed sulfuryl chloride cells are also under investigation [38].

Secondary lithium cells (rechargeable) use propylene carbonate as solvent. Phthalocyanines have proven to be effective catalysts in improving the discharge voltage characteristics of such cells. FePc, CuPc, CoPc, MnPc, AlClPc, ClGaPc, Cl<sub>2</sub>SnPc and metal-free phthalocyanines are among those found to be active. Copper octacyanophthalocyanine and copper poly-phthalocyanine also appear to be useful [39,40]. Secondary cells may also be constructed using metal phthalocyanine polymerically bound to the anode, with zinc as the cathode, and the electrolyte facilitating the I<sub>2</sub>--2I<sup>-</sup> redox reaction, e.g. Fe(III), Co(II), and Cu(II) tetracarboxyphthalocyanines bound to poly(2-vinylpyridine-co-styrene) [41].

#### Biological and Medical Opportunities

Phthalocyaninines are being investigated in the area of photo-toxicity. Thus one might impregnate a cancerous tumour with a phthalocyanine and shine light, perhaps via a laser passed through a fibre optic, onto the site. The phthalocyanine is excited and causes destruction of the tumour. This possibility has great promise as a means of destroying cancerous tumours [42]. Nerves may be 'stained' with a phthalocyanine, and then the nerve energised. Monitoring of the physical properties of the phthalocyanine in such circumstances provides a non-destructive method of probing nerve behaviour [43]. At a more mundane level, staining sutures blue makes them easier to observe inside the

operation site [44]. These various possibilities all rely upon the very low toxicity of MPc systems under normal ground state conditions. Various workers have studied the replacement of heme by metallophthalocyanines in protein environments [45].

#### Miscellaneous

Finally note that substitution of a suitable long chain into metal-free phthalocyanine generates a liquid crystalline material [46], several MPc systems can be induced to lase [47,48] and can be used as phototropic filters for laser applications [48], and electroluminescent diodes can be constructed from phthalocyanine Langmuir-Blodgett films [49]. 'Photochemical hole burning' involves laser irradiation of metal free phthalocyanine at a specific frequency within an inhomogenously broadened absorption line. The result is a persistent reduction in absorption intensity. Such a phenomenon can be used to store information. Thus, via this procedure, phthalocyanines may have value for high density reviews of other uses and features of phthalocyanines, the reader is dire

In this article we have briefly touched upon the considerable interest being shown in phthalocyanines. We confidently expect that this interest will grow and diversify and that phthalocyanines will have a major role to play in industry in the future.

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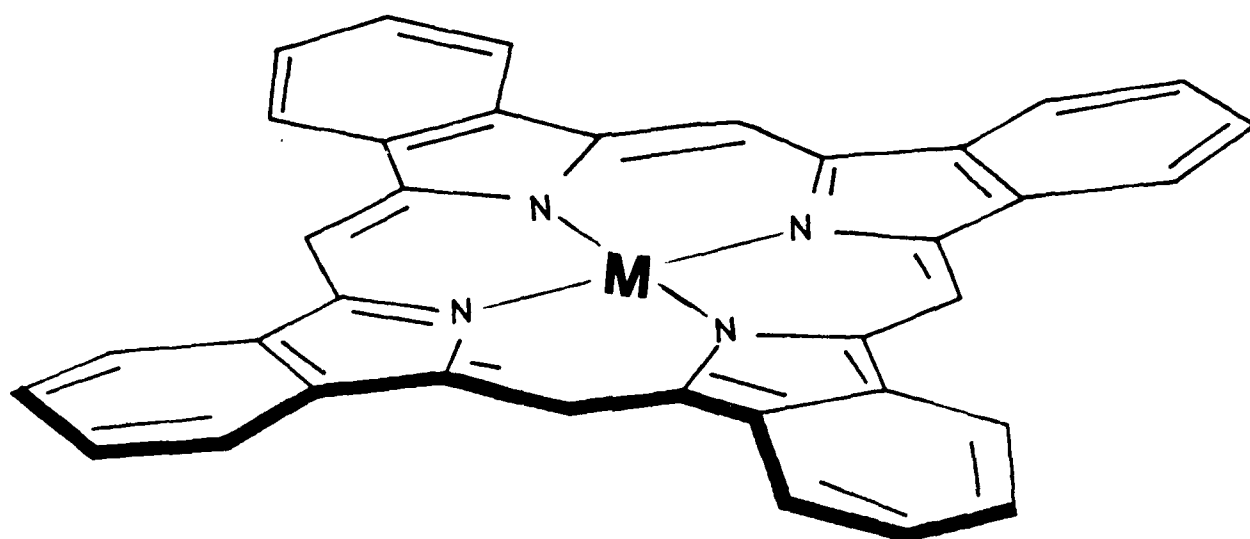
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